

Claims

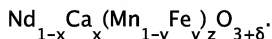
- [c1] 1. A catalyst for use in the electrochemical reduction of oxygen comprising:
- a perovskite-type compound having alpha and beta sites, and having a greater molar ratio of cations at the beta site.
- [c2] 2. The catalyst of claim 1 having the formula $A_{1-x}A'_x(B_{1-y}B'_y)O_{z+3\delta}$ where x, y and z are mole fractions and z is greater than 1.0.
- [c3] 3. The catalyst of claim 1 having the formula $A_{1-x}A'_x(B_{1-y}B'_y)O_{z+3\delta}$ where x, y and z are mole fractions and z is has a range of about 1.0 to about 1.05.
- [c4] 4. The catalyst of claim 2 wherein A is a metal selected from the group consisting of La, Pr and Nd, A' is one or more metals selected from the group consisting essentially of K, Rb, Cs, Ca, Sr, and Ba, B is a metal selected from the group consisting essentially of Mn, and Co, B' is one or more metals selected from the group consisting essentially of Fe, and Ni.
- [c5] 5. The catalyst of claim 4 wherein x has a value in the range of about 0.01 to about 0.9; Y has a value in the

range of about 0.0 to about 0.90; and, δ has a value in the range of about -0.30 to about 0.30.

[c6] 6. The catalyst of claim 1 wherein the cations at the beta site have a smaller crystal ionic radius than the cations at the alpha site.

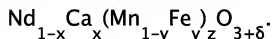
[c7] 7. The catalyst of claim 4 wherein the cations at the beta site have a smaller crystal ionic radius than the cations at the alpha site.

[c8] 8. The catalyst of claim 1 having a composition represented by the formula



[c9] 9. The catalyst of claim 8 wherein x has a value in the range of about 0.01 to about 0.90; y has a value in the range of about 0.0 to about 0.90; and, δ has a value in the range of about -0.3 to about 0.30, and z has a range of about 1.0 to about 1.05.

[c10] 10. A catalyst for use in the electrochemical reduction of oxygen having a composition represented by the formula



[c11] 11. The catalyst of claim 10 wherein x has a value in the range of about 0.01 to about 0.9; y has a value in the range of about 0.0 to about 0.9; δ has a value in the

range of about -0.3 to about 0.3 .

- [c12] 12. The catalyst of claim 11 wherein z has a range of about 0.95 to about 1.05 .
- [c13] 13. The catalyst of claim 10 wherein z is greater than 1.0 .
- [c14] 14. The catalyst of claim 10 wherein x has a value in the range of about 0.1 to about 0.60 ; y has a value in the range of about 0.0 to about 0.40 ; and, δ has a value in the range of about -0.3 to about 0.30 and z has a value from about 0.95 to about 1.05 .
- [c15] 15. The catalyst of claim 10 wherein z has a range of about 1.0 to about 1.02 .
- [c16] 16. The catalyst of claim 10 wherein x has a value in the range of about 0.2 to about 0.50 .
- [c17] 17. The catalyst of claim 10 wherein y has a value in the range of about 0.0 to about 0.30 .
- [c18] 18. A method for diffusing a catalyst with carbon for use in a gas diffusion electrode reaction layer, the method comprising the steps of:
- preparing an aqueous solution containing (a) metal salts at a predetermined molar ratio and (b) carbon;
 - heating the aqueous solution in a non-oxidizing at-

mosphere to a gel and further heating gel to form a char; and,
calcining the char.

[c19] 19. The method of claim 18 including the step of mixing a quantity of the desired oxide catalyst with the carbon before adding the carbon to the aqueous solution, the amount of premixed metal oxide is chosen in conjunction with the amount of metal salts to provide the desired molar ratio after calcining.

[c20] 20. The method of claim 18 wherein the carbon is in the form of fine particle carbon black having a BET specific surface area of 30 to 2,000 m²/g.

[c21] 21. The method of 18 wherein the catalyst has the formula $A_{1-x}A'_x(B_{1-y}B'_y)_zO_{3+\delta}$ the metal is selected from the group consisting essentially of La, Pr and Nd; A' is one or more metals selected from the group consisting essentially of K, Rb, Cs, Ca, Sr, and Ba; B is a metal selected from the group consisting essentially of Mn, and Co; B' is one or more metals selected from the group consisting essentially of Fe, and Ni.

[c22] 22. The method of claim 21 wherein the carbon is in the form of fine particle carbon black having a BET specific surface area of 30 to 2,000 m²/g.

[c23] 23. The method of claim 18 wherein the resulting catalyst is represented by the formula $\text{Nd}_{1-x}\text{Ca}_x(\text{Mn}_{1-y}\text{Fe}_y)_z\text{O}_{3+\delta}$.

[c24] 24. The method of claim 23 wherein x has a value in the range of about 0.01 to about 0.90; y has a value in the range of about 0.0 to about 0.90; and, δ has a value in the range of about -0.3 to about 0.30.

[c25] 25. The method of claim 24 wherein z has a range of about 0.95 to about 1.05.

[c26] 26. The method of claim 23 wherein x has a value in the range of about 0.1 to about 0.60; y has a value in the range of about 0.0 to about 0.40; and, δ has a value in the range of about -0.3 to about 0.30 and z has a value from about 0.95 to about 1.05.

[c27] 27. The method of claim 23 wherein x has a value in the range of about 0.2 to about 0.50.

[c28] 28. The method of claim 23 wherein y has a value in the range of about 0.0 to about 0.30.

[c29] 29. The method of claim 18, wherein the carbon is selected from the group consisting essentially of acetylene black, furnace black, channel black, and thermal black.

- [c30] 30. The method of claim 19, wherein the carbon is selected from the group consisting essentially of acetylene black, furnace black, channel black, and thermal black.
- [c31] 31. The method of claim 21, wherein the carbon is selected from the group consisting essentially of acetylene black, furnace black, channel black, and thermal black.
- [c32] 32. A gas diffusion electrode for electrochemical reduction of oxygen comprising:
 a least one reaction layer having dispersed therein a perovskite-type catalyst having alpha and beta sites and having a greater molar ratio of cations at the beta site.
- [c33] 33. The gas diffusion electrode of claim 32 wherein the catalyst having the formula $A_{1-x}A'_x(B_{1-y}B'_y)_zO_{3+\delta}$ here x, y and z are mole fractions and z is greater than 1.0.
- [c34] 34. The gas diffusion electrode of claim 32 wherein the catalyst having the formula $A_{1-x}A'_x(B_{1-y}B'_y)_zO_{3+\delta}$ here x, y and z are mole fractions and z is has a range of about 1.0 to about 1.05.
- [c35] 35. The gas diffusion electrode of claim 33 wherein A is a metal selected from the group consisting of La, Pr and Nd, A' is one or more metals selected from the group consisting essentially of K, Rb, Cs, Ca, Sr, and Ba, B is a

metal selected from the group consisting essentially of Mn, and Co , B' is one or more metals selected from the group consisting essentially of Fe, and Ni.

- [c36] 36. The gas diffusion electrode of claim 35 wherein x has a value in the range of about 0.01 to about 0.9; Y has a value in the range of about 0.0 to about 0.90; and, δ has a value in the range of about -0.30 to about 0.30.
- [c37] 37. The gas diffusion electrode of claim 36, wherein the catalyst is dispersed with carbon black selected from the group consisting essentially of acetylene black, furnace black, channel black, and thermal black.
- [c38] 38. The gas diffusion electrode of claim 33 wherein the cations at the beta site have a smaller crystal ionic radius than the cations at the alpha site.
- [c39] 39. The gas diffusion electrode of claim 32 wherein the cations at the beta site have a smaller crystal ionic radius than the cations at the alpha site.
- [c40] 40. The gas diffusion electrode of claim 32 where a portion of the perovskite type oxide was thermally heated in the presence of a non-oxidizing atmosphere.
- [c41] 41. The gas diffusion electrode of claim 32, wherein the catalyst is dispersed with carbon black selected from the

group consisting essentially of acetylene black, furnace black, channel black, and thermal black.

- [c42] 42. The gas diffusion electrode of claim 41 wherein the catalyst and the carbon are bonded by a hydrophobic binder polymer selected from the group consisting essentially of PTFE, FEP, PFA, ETFE, and PCTFE.
- [c43] 43. The gas diffusion electrode of claim 32 where a portion of the perovskite-type oxide was synthesized from a solution containing metal salts.
- [c44] 44. The gas diffusion electrode of claim 32 including an interface to an alkaline electrolyte.
- [c45] 45. A gas diffusion electrode for electrochemical reduction of oxygen comprising:
a least one reaction layer having dispersed therein a perovskite-type compound having a composition represented by the formula
$$\text{Nd}_{1-x}\text{Ca}_x(\text{Mn}_{1-y}\text{Fe}_y)_z\text{O}_{3+\delta}.$$
- [c46] 46. The gas diffusion electrode of claim 45 wherein x has a value in the range of about 0.01 to about 0.9; y has a value in the range of about 0.0 to about 0.9; δ has a value in the range of about -0.3 to about 0.3.
- [c47] 47. The gas diffusion electrode of claim 46 wherein z

has a range of about 0.95 to about 1.05.

[c48] 48. The gas diffusion electrode of claim 45 wherein z is greater than 1.0.

[c49] 49. The gas diffusion electrode of claim 45 wherein x has a value in the range of about 0.1 to about 0.60; y has a value in the range of about 0.0 to about 0.40; and, δ has a value in the range of about -0.3 to about 0.30 and z has a value from about 0.95 to about 1.05.

[c50] 50. The gas diffusion electrode of claim 46 wherein z has a range of about 1.0 to about 1.02.

[c51] 51. The gas diffusion electrode of claim 46 wherein x has a value in the range of about 0.2 to about 0.50.

[c52] 52. The gas diffusion electrode of claim 46 wherein y has a value in the range of about 0.0 to about 0.30.

[c53] 53. The gas diffusion electrode of claim 45 wherein the catalyst and the carbon are bonded by a hydrophobic binder polymer selected from the group consisting essentially of PTFE, FEP, PFA, ETFE, and PCTFE.

[c54] 54. The gas diffusion electrode of claim 53, wherein the catalyst is dispersed with carbon black selected from the group consisting essentially of acetylene black, furnace black, channel black, and thermal black.

- [c55] 55. The gas diffusion electrode of claim 48 wherein the catalyst and the carbon are bonded by a hydrophobic binder polymer selected from the group consisting essentially of PTFE, FEP, PFA, ETFE, and PCTFE.
- [c56] 56. The gas diffusion electrode of claim 45 where a portion of the perovskite-type oxide was synthesized from a solution containing metal salts.
- [c57] 57. The gas diffusion electrode of claim 45 where a portion of the perovskite type oxide was thermally heated in the presence of a non-oxidizing atmosphere.
- [c58] 58. The gas diffusion electrode of claim 45 including an interface to an alkaline electrolyte.
- [c59] 59. The gas diffusion electrode of claim 44 including an interface to an alkaline electrolyte.
- [c60] 60. The gas diffusion electrode of claim 47 including an interface to an alkaline electrolyte.
- [c61] 61. The gas diffusion electrode of claim 49 including an interface to an alkaline electrolyte.